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Ethyl lactate from dihydroxyacetone by a montmorillonite-supported Pt(II) diphosphane complex

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ABSTRACT

The Lewis-acidity of a series of bis-cationic Pt(II)(aqua) complexes bearing phosphane ligands was exploited to catalyze the conversion of dihydroxyacetone to ethyl lactate. The Pt(II) complex bearing 1, 2-bis(diphenylphosphanyl)ethane and triflate as counter anion showed high catalytic activity (TOF = 530 h^{-1}) and chemoselectivity (>96%) at 70 °C. On intercalating the latter precatalyst between the lamellae of Na-montmorillonite by a cationic exchange process, high chemoselectivity for ethyl lactate (>99%) at 70 °C was observed, which was maintained in three consecutive catalytic runs.

1. Introduction

Ethyl lactate (EtLA) is an environmentally benign solvent which finds its major application: (i) in the coating industry as a result of its high solvency power, high boiling point, low vapor pressure and low surface tension; (ii) as cleaning agent for the polyurethane industry and for metal surfaces, from which the removal of greases, oil adhesives and solid fuels is allowed; and (iii) in the pharmaceutical industry as a solvent for various biologically active compounds [1]. EtLA is conventionally produced via esterification of lactic acid with ethanol in the presence of an acid catalyst. The main drawback of this method is the self-esterification of lactic acid which leads to a mixture of acid and ester monomer and oligomers. Alternative synthetic protocols for EtLA use glycerol [2], C_6 [3,4] and C_3-sugars, such as glyceraldehyde or dihydroxyacetone (DHA) [5–12] as starting material. DHA is a convenient starting compound, since it is obtained by either fermentation of glycerol [13] or selective metal-based glycerol oxidation reactions [14–19]. Homogeneous metal salt-based catalytic reactions employed for the DHA to alkyl lactate conversion occurred only at a high metal concentration (ca. 10 mol%). In the case of $SnCl_2$, which is one of the most promising Lewis acid-based precatalysts for DHA to EtLA conversion, the resulting chemoselectivities for EtLA are <90% at 90 °C [5]. Sn-modified zeolites and montmorillonite (MMT) showed EtLA chemoselectivity >90% at 90 °C [6] and 150 °C [8], respectively. Pyruvaldehyde diacetal (PADA) was found to be the main side product, which is, in case of Sn-based catalysts, slowly converted to EtLA at high reaction temperatures [8]. The highest chemoselectivity for EtLA (96%), although with a low catalytic activity, has been reported for an amorphous mesoporous alumosilicate with a Si to Al atom ratio of 10 [11]. MMT is an alumosilicate clay mineral well known to constitute a suitable support for Pt-nanoparticles (NPs) [20] and Pt-coordination compounds [21]. These systems have been successfully used as catalysts for hydrogenation of nitro compounds to the corresponding anilines.

We exploited the Lewis-acidity of well-defined cationic Pt(II) (aqua)diphosphane complexes [22–24] for the catalytic conversion of DHA to EtLA in both homogeneous and heterogeneous (MMT-intercalated) phases. The confinement of the Pt-based catalyst between the lamellae of MMT, led to a significant increase in the catalytic activity and chemoselectivity.

2. Experimental

2.1. Materials

All reagents used were purchased from Aldrich. Na-MMT (cation exchange capacity of 128 meq./100 g) was purchased from

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Laviosa Chimica Mineraria (Italy). *Meso*-2,4-bis(diphenylphosphino)pentane (bdppp) was synthesized as described in the literature [25]. Solvents used for synthesis and catalysis were distilled over an appropriate drying reagent, while deuterated ones were used as received.

2.2. Physical methods used

^{31}P {^{1}H} and ^{1}H NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer at 161.98 and 400.13 MHz, respectively.

FTIR spectra of synthesized complexes were acquired on a Perkin Elmer BX instrument using KBr pellets.

Powder X-ray diffraction (PXRD) experiments were carried out with a PANalytical X'PERT PRO powder diffractometer, employing Cu Kα (λ = 1.5418 Å) radiation and a parabolic MPD-mirror. Diffractograms were acquired in the 2θ range from 1.0 to 60.l0°, applying a step size of 0.0263° and a counting time of 88.7 s.

Transmission electron microscopy (TEM) analysis of the recovered catalyst was carried out with a ZEISS LIBRA 200FE High-resolution Transmission Electron Microscope (HRTEM), equipped with a FEG source operating at 200 KV. The sample was prepared by vigorously rubbing the solid between two clean glass slides, and it was then dispersed onto holey-carbon films, supported on a copper grid (300 mesh) by adherence.

X-ray photoelectron spectroscopic (XPS) investigation was carried out in an ultrahigh vacuum system (UHV, base pressure 10^{-9} -mbar) equipped with a VSW HAC 500 hemispherical electron-energy analyzer operating in the constant analyzer energy mode (CAE) at pass energy E_{pas} = 22 eV with a step size of 1.0 and 0.1 eV respectively for survey and high-resolution spectra mode. A non-monochromatic Mg K_{α} source operating at 120 W power (10 kV × 10 mA) was employed as X-ray source. No compensation for charging effect was applied and the Binding Energy (BE) values were scaled using C 1s (284.8 ± 0.1 eV) of adventitious carbon as an internal standard. The samples were deposited in the sample holder as thin powder layers onto a vacuum-grade carbon tape, introduced in the UHV system via a loadlock and kept in the preparation chamber at least overnight in order to allow the volatile substance to evaporate. The XPS peaks were fitted using CasaXPS software employing Gauss-Lorentz curves after subtraction of a Shirley-type background.

ICP-OES analyses of the supported catalyst and of the catalytic solution were carried out with an iCAP 6200 Duo upgrade, Thermofisher instrument. 11.2 mg of the supported catalyst and 5.0 mL of catalytic solution were separately heated in a porcelain crucible and treated with aqua regia (4 × 2 mL) for four times, dissolving the solid residue in 0.5 M aqueous HCl. The limit of detection (lod) calculated for platinum was 0.01 ppm.

Lewis and Brønsted acid sites in Na-MMT and Pt(dppe)@MMT were quantified by pyridine adsorption and FTIR spectroscopy, applying the following procedure: the sample was pressed in a 13-mm diameter pellet, placed in a glass IR cell with CaF_2 windows and pretreated at 150 °C for 1 h in vacuum, followed by contacting it with pyridine vapor for 10 min. at room temperature and degassing it for 30 min. Pyridine desorption was achieved by heating up the sample until 250 °C. Spectra were recorded at room temperatures 50, 100, 150, 200 and 250 °C. The acidity was calculated according to literature reports [26]. IR spectra elaboration was performed with the Origin software and peak deconvolution was carried out applying a Gaussian-type peak fitting procedure.

GC-FID analyses of the catalytic solutions were carried out with a Shimadzu 2010 instrument, equipped with a FID detector and a VF-WAXms capillary column (30 m, 0.25 mm (i.d.), 0.25 μm (film thickness)) using He as carrier gas.

2.3. Preparation of Pt(II) diphosphane complexes

In a round bottomed flask, K_2PtCl_4 (103.8 mg, 0.250 mmol) was dissolved in degassed acetonirile (15.0 mL). To this suspension was added the desired phosphane ligand (0.250 mmol (diphosphane) or 0.500 mmol (PPh_3)). The obtained suspension was stirred over night at 50 °C. Afterward the solvent was removed completely and the residue washed with water in order to remove KCl. The obtained off-white solids were dried under vacuum giving in the case of 1,1′-bis(diphenylphosphanyl)ferrocene (dppf), *meso*-bdppp, bis(diphenylphosphanyl)methane (dppm) and PPh_3 the corresponding $PtCl_2$ complexes in 70–80% yield. In case of 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,2-bis(diphenylphosphanyl)benzene (benzphos) $[Pt(PP)_2]$ $(PtCl_4)$ was obtained as major compound, showing a characteristic $^{1}J_{PtP}$ of ca. 2380 Hz. Upon heating of these Magnus type-salts in degassed DMF at 110 °C for 4 h, complete conversion to the corresponding $PtCl_2$(PP) compound was achieved. The obtained $PtCl_2$(PP) complexes (0.200 mmol) were dissolved in degassed CH_2Cl_2, distilled over CaH_2 under a nitrogen atmosphere. Afterward, AgX (X = Otf^-, OTs^- or PF_6^-) was added and the reaction continued at room temperature under a nitrogen atmosphere and under exclusion of light. After a reaction time of 2 h, the suspension was filtered through a celite path and the obtained clear solution concentrated to dryness. The obtained cationic Pt(II)-aqua complexes (1a-6a, 3b and 3c) were isolated as off-white solids in 60–75% yield. Characteristic ^{31}P{^{1}H} NMR chemical shifts (δ) and $^{1}J_{PtP}$ coupling constants of the latter complexes are compiled in Table 1. Even using CaH_2-destilled CH_2Cl_2, traces of water are introduced in the reaction vessel by weighting the hygroscopic silver salts in air atmosphere.

$[Pt(dppe)(Py)_2](Otf)_2$ was synthesized by reaction of a solution of $PtCl_2$(dppe) (139.8 mg, 0.210 mmol) in deareated CH_2Cl_2 (30.0 mL) with silver triflate (18.1 mg, 0.421 mmol) in the presence of pyridine (35.7 μL, 0.442 mmol) at room temperature for 1 h. Afterward the obtained suspension was passed through celite and the resulting solution concentrated to a small volume (3.0 mL). After addition of diethyl ether (25.0 mL) the product precipitated as off-white solid, which was separated by filtration and dried in a stream of nitrogen. Yield: 176.3 mg, 80%.

^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$, 20 °C, ppm): δ = 35.31 (s, $^{1}J_{PtP}$ = 3246 Hz). ^{1}H NMR (400.13 MHz, $CDCl_3$, 20 °C, ppm): δ = 2.93 (m, 4H, CH_2CH_2), 7.21–8.98 (m, 30H, Ar-H). FTIR spectrum is shown in Fig. S1.

2.4. Preparation of Pt(dppe)@MMT

Na-MMT (300.0 mg) was dispersed in a degassed 3:1 (v:v) EtOH-water mixture (40.0 mL) at 50 °C for 1 h. Then 3a

Table 1
^{31}P{^{1}H} NMR data for $PtCl_2PP$ and $[Pt(H_2O)_2(PP)](Otf)_2$ compounds.

Phosphane	$PtCl_2$(PP) δ (ppm), $^{1}J_{PtP}$ (Hz), solvent	$[Pt(H_2O)_2(PP)](Otf)_2$ δ (ppm), $^{1}J_{PtP}$ (Hz), solvent
dppf	12.9, (3779), CD_2Cl_2 [27]	9.2, (4206), CD_2Cl_2 (1a) [27]
meso-bdppp	10.2, (3420), $CDCl_3$	3.4, (3680), DMSO-d_6 (2a)
dppe	41.9, (3623), CD_2Cl_2	36.3, (3979), CD_2Cl_2 (3a) [28]
		34.0, (4024), $CDCl_3$[a] (3b)
		35.8, (4075), $CDCl_3$[b] (3c)
benzphos	40.8, (3610), $CDCl_3$	32.5, (4089), $CDCl_3$ (4a)
dppm	−63.2, (3058), DMF-d_7 [29]	-68.5, (3351), CD_2Cl_2 (5a)
PPh_3	14.4, (3673), $CDCl_3$ [30]	3.2, (4172), $CDCl_3$[c] ($6a_{cationic}$)
		5.3, (4056), $CDCl_3$[c] ($6a_{neutral}$)

[a] OTs^- as counter anion.

[b] PF_6^- as counter anion.

[c] Isomers with *cis*-PPh_3 coordination at Pt(II) ($6a_{cationic}$ and $6a_{neutral}$ in a 1:2 molar ratio).